UPPER GREAT LAKES CONNECTING CHANNELS
INTERLABORATORY PERFORMANCE EVALUATION STUDY
INTEGRATED REPORT
PART II: TRACE METALS

by
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ABSTRACT

The Upper Great Lakes Connecting Channels (UGLCC) Study recognizes Quality Assurance/Quality Control (QA/QC) aspects as crucial elements to the overall utility of study results. As part of the QA/QC program, thirteen interlaboratory performance evaluation studies were designed and conducted by the Quality Management Work Group.

Thirteen individual final reports on these interlaboratory studies have been completed. In addition, two integrated reports, one for organic parameters, and the other for trace metals, have been generated. These reports summarize and evaluate these interlaboratory studies. This report deals with overall interlaboratory results of trace metals conducted in QM-3, QM-5 and QM-9. The interlaboratory comparability of trace metals for accuracy and precision was evaluated and the relative performance of participating laboratories for trace metals was categorized to assist the project leaders, managers and users of data in evaluation of their client laboratories.

1.0 INTRODUCTION

The Upper Great Lakes Connecting Channel Study (UGLCCS) was established to identify and deal with the environmental problems involved with the St. Mary's, St. Clair and Detroit Rivers and Lake St. Clair. A three-year, binational study was started in 1984, involving Canadian and U.S. environmental and resource agencies.

The UGLCC Study recognizes Quality Assurance/Quality Control (QA/QC) aspects as crucial elements to the overal utility of study results. The Quality Management Work Group was formed and as part of its QA program, thirteen interlaboratory performance evaluation (QC) studies were designed and conducted to assist analytical laboratories, which are producing data for the UGLCC Study, to generate reliable, accurate data and to assess their overall performance during this study.

Thirteen individual final reports on these interlaboratory studies have been completed, as listed in Appendix I. To further assist the project leaders, managers and users of data in their evaluation of the comparability of data generated by their laboratories, two integrated reports, one for organic parameters and the other for trace metals, have been generated. These reports summarize and evaluate the accuracy and precision of interlaboratory comparability of those thirteen studies. This report will deal with the overall interlaboratory results of trace metals in sediments and waters conducted in the QM-3, QM-5 and QM-9 interlaboratory studies.

2.0 STUDY DESIGN

To support the Upper Great Lakes Connecting Channels Study, the Quality Management Work Group (QMWG) was formed, in part, to design and conduct interlaboratory performance evaluation studies. For trace metals, the interlaboratory studies were conducted in studies QM-3 for trace metals in sediments, QM-5 for trace metals in surface waters and QM-9 for total mercury in surface waters.

The participants in these studies were from different governmental and private laboratories. See Table 1 for the list of participants .

Each participating laboratory in QM-3 was sent five sediment samples. These sediment samples were to be analyzed for 10 elements, namely Cd, Pb, Zn, Cu, Ni, Hg, Co, Fe, Cr and Se. Each participating laboratory in QM-5 was sent four surface water samples with blind duplicate pairs. These water samples were to be analyzed for 7 elements, namely Cd, Pb, Zn, Cu, Ni, Co and Fe. While for QM-9, each participating laboratory was sent four water samples with duplicate pairs for analysis of total mercury only.

All studies were prepared and distributed from the facility of the Research and Applications Branch at the National Water Research Institute in Burlington.

3.0 DATA EVALUATION

For the interlaboratory comparability, the accuracy of interlaboratory results was evaluated by the recoveries of the interlaboratory medians based on the design values. Medians rather than means were preferred when there were relatively few data and means were strongly influenced by outliers. The precision of interlaboratory results was evaluated by the relative standard deviations (RSDs) with the outliers removed by Grubbs' test (1). To estimate the analytical precision of each laboratory, the within-lab precision for each parameter was calculated based on the blind duplicate pairs for RSDs. See Appendix II for a summary of within-lab precision for each participating laboratory.

In addition, for the evaluation of laboratory performance, results received from these interlaboratory studies were evaluated by Youden's ranking technique (2) for the detection of bias, as well as a computerized flagging procedure (3). A laboratory's results were judged biased high or low, when its total rank was outside of a statistical allowable range. Results were flagged very low, low, high or very high, when they deviated significantly from the interlaboratory medians. In the case of Cd and Cr in QM-3, when the medians deviated significantly from the design values, the flagging was based on the design values rather than the medians. For a further explanation of the ranking and flagging procedures, see Appendix III. This statistical procedure, which semi-quantitatively evaluates data accuracy and precision is widely used in other interlaboratory QA studies (4,5). See Appendix IV for a summary of the bias and flag statements for trace metals in various studies. These results are summarized from the final reports of QM-3, QM-5 and QM-9.

4.0 RESULTS AND DISCUSSION

The interlaboratory comparability of trace metals for accuracy and precision, and the comparison of laboratory performance in various studies are discussed below.

4.1 Interlaboratory Comparability

The design values and interlaboratory medians for trace metals are summarized in Tables 2 and 3 for sediments and waters, respectively. In order to determine the bias of interlaboratory results, the range and average values of percent recoveries of interlaboratory medians for all samples reported in various studies are also summarized in Table 4. Figs. 1 and 2 present graphically condensed results of the range and average values of percent recoveries of interlaboratory medians for all elements analyzed and all samples reported in sediments and waters, respectively. For the sediment samples analyzed in QM-3, seven out of the 10 elements determined, namely Pb, Zn, Hg, Cu, Ni, Co and Fe, were satisfactory not only with average recoveries for all samples tested within ± 25 % of the design values, but also the ranges of recoveries for all samples were within ±25 % of the design values. As part of the QMWG recommendation for a QC/QA program for UGLCCS, values determined for QC samples should fall within a window of ±25 % of the design values in order to be satisfactory. The performance of Cd and Se for these sediment samples were satisfactory with average recoveries for all samples within ±25 % of the design values, but the ranges of recoveries for all samples tested showed wide variations and fell outside the window of ±25 % of the design values. The interlaboratory results for Cr were less satisfactory with average recovery for all samples exceeding ±25 % of the design value, presumably due to incomplete digestion of the sediment samples.

For the water samples analyzed in QM-5 and QM-9 as shown in Fig. 2, the interlaboratory comparability was excellent. All seven elements, namely Cd, Pb, Zn, Cu, Ni, Co and Fe, determined in QM-5 and Hg in QM-9 were satisfactory with the ranges and averages of interlaboratory medians for all samples within ±25 % of the design values. Relatively, the ranges of recoveries among test samples had wider variations for Zn and Hg than those obtained for the remaining elements.

Comparing Fig. 1 and Fig. 2 for sediment and water samples, the ranges of recoveries for water samples were smaller than those for sediment samples in most cases. In these interlaboratory studies, sediment samples were digested by dissolution before AAS or ICP detection. Thus, they were subject to wide variations attributable to contamination, loss of analytes or incomplete digestion. While water samples were analyzed directly without sample preparation except for Hg which required digestion.

Precision of interlaboratory results for trace metals in various studies is summarized in Table 5. Figs. 3 and 4 present graphically condensed results of the ranges and averages of RSDs for all samples analyzed in sediments and waters, respectively. For the sediment samples, five out of the 10 elements, namely Pb, Zn, Cu, Ni and Fe had average RSDs within ±25 %. These five elements also exhibited smaller ranges of RSDs for all samples as compared with the other remaining 5 elements. Especially, Cr and Se showed the wide ranges of RSDs for all tested samples and the average RSDs for these two elements were more than ±50 %. While for the water samples, as shown in Fig. 4, all seven elements (namely Cd, Pb, Zn, Cu, Ni, Co and Fe) determined in QM-5 were very satisfactory not only with the average RSDs for all samples better than ±25 %, but the ranges of RSDs for all samples were within ±25 %. While Hg determined in QM-9 showed a wide range of RSDs among test samples and the average RSD for all samples analyzed was more than ±25 %.

Overall, comparing the precision of interlaboratoy results for sediment and water samples, the less scattered results among test samples were obtained for water samples than those obtained for sediment samples except Hg. The wider variations of RSD for Hg among test samples for water samples as compared with those for sediment samples, perhaps, was attributed to the lower concentrations of Hg in these water samples.

In general, the interlaboratory comparability for the accuracy and precision of trace metals in sediment and water samples was satisfactory in most cases.

Within-lab precision was evaluated only for water samples, as summarized in Appendix II. In most cases, the within-lab precision in QM-5 had the average RSDs within ±10 % except Fe from U075. While for Hg in QM-9, there were average RSDs more than ±10 % from several laboratories (U001, U010, U057 and U078). However, all these within-lab average RSDs were smaller than the interlaboratory average RSD (37.2 %).

4.2. Comparison of Laboratory Performance

The key to administering information involving the laboratory performance data is the selection of acceptance criteria. The performance evaluation of trace metals in this report is based on the percent biased of parameters analyzed and percent flagged of results reported. For the flags, the number of results reported by each laboratory excluding those with "ND", "NS" or "LT" codes, the sum of results flagged with VH, H, L or VL for all parameters, and the percentages flagged are calculated. Note that H and L flags are counted as half of VH and VL flags. In addition, less than values that were flagged are included in the calculation of the percent flagged. For the bias, the number of parameters analyzed by each laboratory, the sum of parameters biased with H or L based on Youden's ranking technique, and the percent of parameters biased are calculated.

The above criteria can be used independently in evaluating the laboratory performance of interlaboratory results on accuracy or precision. To simplify the overall assessment of laboratory performance in various studies, the average of percent biased and percent flagged is calculated. This criteria of performance index provides a simple way to compare the relative performance of participating laboratories in various studies as shown below:

Average of % Biased and % Flagged (%)	Comment
≤ 25 %	Satisfactory (A)
26 - 50 %	Moderate (B)
> 50 %	Poor (C)

Results of the above-mentioned criteria for trace metals in various studies are summarized in Table 6. As shown in this table, several laboratories (U001, U057, U077, U078 and U091) have provided consistent and satisfactory results for the interlaboratory studies in which they participated. On the other hand, few laboratories provided poor results in some of the interlaboratory studies in which they participated, such as U075 and U079 for QM-9 and U096 for QM-3.

The participating laboratories, categorized from satisfactory to poor for sediments and waters, are summarized in Tables 7 to 9 for QM-3, QM-5 and QM-9, respectively. As shown in Table 7 for QM-3, overall, laboratory U001 had the most accurate results with the lowest value (6.1 %) for the performance index (average of %

biased and % flagged). On the other hand, laboratory U096 had the highest value (57.5 %) of the performance index.

As shown in Table 8 for QM-5, laboratory U001 (both U001A and U001B) had the best performance index without any bias or flags. While U096 again had the highest value (43.8 %).

Whereas for QM-9 as shown in Table 9, several laboratories (U001, U014, U077 and U091) had the best performance index for total Hg with no bias and no flags. On the other hand, U075 had the highest value (100 %) wtih this parameter biased and all the results flagged. These results provided the additional information for project leaders, managers and users of data on the comparability of their client laboratories.

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TABLE 1

Participants in Trace Metal's Interlaboratory Performance Evaluation Studies

Lab Code	Study Number QM-3	QM-5	QM-9
U001	x	x	x
U005	x	-	-
U010	x	x	x
U014	x	x	x
U049	x	x	x
U057	x	x	x
U075	x	x	x
U077	-	x	x
U078	-	-	x
U079	-	x	x
U091	-	x	x
U096	x	x	-

Note: x: participated
-: not participated

Table 2. Design values and interlaboratory medians for trace metals in Sediments ~~(from Data Summary)~~. All values are in ug/g, except iron (%).

Parameter	WQB-1 Sample 301		WQB-3 Sample 302		TH-1 Sample 303		HR-1 Sample 304		SUD REF-1 Sample 305	
	Design Value	Median	Design Value	Median	Design Value	Median	Design Value	Median	Design Value	Median
Cadmium	1.85	2.00	3.2	3.00	5.9	6.40	4.3	3.50	1.8	4.00
Lead	83.9	82.0	230	233	260	264	146	148	53.4	66.0
Zinc	277	289	1430	1260	1601	1450	1157	1060	825	710
Mercury	1.09	1.00	2.7	2.70	0.44	0.48	0.35	0.35	0.094	0.10
Copper	78.7	79.5	80	81.0	106	102	80.5	81.1	579	540
Nickel	63.8	*54.0	55	*48.5	42.0	*42.5	36.4	*33.1	933	* 820
Cobalt	18.2	19.0	14.8	13.0	15.2	15.2	13.0	13.0	44.8	41.1
Iron	5.06	4.44	6.2	5.90	3.70	3.40	3.36	2.70	3.46	3.00
Chromium	104	*63.0	160	* 100	139	* 120	138	* 118	99.7	*71.0
Selenium	1.02	0.88	1.9	1.00	0.49	0.61	0.50	0.48	2.2	2.24

* Data from laboratory U096 are not included in these calculations.

TABLE ~~2~~ 3

Design Values and Interlaboratory Medians for Trace Metals in Waters
(All values are in ug/ℓ)

Parameter	Design Value	Interlab. Median Sample 501	Interlab. Median Sample 504	Design Value	Interlab. Median Sample 502	Interlab. Median Sample 503
Iron	499	520	510	166	170	170
Cobalt	297	296	290	99.0	100	100
Nickel	481	490	484	160	168	168
Copper	103	110	110	34.0	36.0	36.0
Zinc	108	107	100	36.0	34.0	37.0
Cadmium	98.0	97.0	96.0	33.0	32.0	33.0
Lead	485	487	491	162	164	161

TABLE 3 (Continued)

Design Values and Interlaboratory Medians for Total Mercury in Waters

(all values are in ug/l)

Parameter	Design Value	Interlab. Median Sample 901	Interlab. Median Sample 904	Design Value	Interlab. Median Sample 902	Interlab. Median Sample 903
Total Mercury	0.60	0.575	0.570	0.24	0.250	0.260

TABLE 4

Range and Average Values of Percent Recoveries for the Trace Metals in Various Studies

Parameter	QM-3 (Sediments)		QM-5 (Waters)		QM-9 (Waters)	
	Range	Average	Range	Average	Range	Average
Cd	81.4-222	123 (5)	97.0-100	98.5 (4)	--	--
Pb	97.7-124	105 (5)	99.4-101	100 (4)	--	--
Zn	86.1-104	92.1 (5)	92.6-103	97.3 (4)	--	--
Hg	91.7-109	101 (5)	--	--	95.0-108	101 (4)
Cu	93.3-101	98.5 (5)	106-107	107 (4)	--	--
Ni	84.6-101	90.5 (5)	101-105	103 (4)	--	--
Co	87.8-104	96.7 (5)	97.6-101	99.8 (4)	--	--
Fe	80.4-95.2	88.4 (5)	102-104	103 (4)	--	--
Cr	60.6-86.3	73.2 (5)	--	--	--	--
Se	52.6-124	92.2 (5)	--	--	--	--

Note: The numbers in parentheses are the number of samples.

TABLE 5

Range and Average Values of RSDs for the Trace Metals in Various Studies

Parameter	QM-3 (Sediments)		QM-5 (Waters)		QM-9 (Waters)	
	Range	Average	Range	Average	Range	Average
	%					
Cd	44.1-70.0	55.8 (5)	6.4-8.4	7.4 (4)	--	--
Pb	13.3-27.5	21.5 (5)	4.5-12.2	7.9 (4)	--	--
Zn	6.6-14.2	10.3 (5)	7.3-10.5	8.8 (4)	--	--
Hg	17.5-34.2	25.8 (5)	--	--	13.6-57.4	37.2 (4)
Cu	5.2-10.0	8.2 (5)	11.5-15.7	13.5 (4)	--	--
Ni	18.2-24.4	21.0 (5)	5.4-12.0	8.8 (4)	--	--
Co	11.2-37.0	26.2 (5)	5.2-10.8	7.8 (4)	--	--
Fe	18.8-37.2	24.3 (5)	5.9-14.8	9.1 (4)	--	--
Cr	15.3-38.5	25.8 (5)	--	--	--	--
Se	12.4-91.8	54.9 (5)	--	--	--	--

Note: The numbers in parentheses are the number of samples.

TABLE 6

Comparison of Laboratory Performance for TMs in Various Studies

Lab No.	Study No.	Matrix	Bias: No. of Parameters Analysed	Bias: No. of Parameters Biased	Bias: % of Parameters Biased	Flags: No. of Results Reported	Flags: No. of Results Flagged	Flags: % of Results Flagged	Average of % Biased and % Flagged	Comment
U001	QM-3	Sediments	8	0	0.0	41	5.0	12.2	6.1	A
	QM-9	Waters	1	0	0.0	4	0.0	0.0	0.0	A
U001A	QM-5	Waters	7	0	0.0	28	0.0	0.0	0.0	A
U001B	QM-5	Waters	7	0	0.0	28	0.0	0.0	0.0	A
U005	QM-3	Sediments	10	2	20.0	50	20.0	40.0	30.0	B
U010	QM-3	Sediments	10	3	30.0	50	17.5	35.0	32.5	B
	QM-5	Waters	7	2	28.6	28	3.5	12.5	20.6	A
	QM-9	Waters	1	0	0.0	4	1.0	25.0	12.5	A
U014	QM-3	Sediments	10	3	30.0	46	13.5	29.3	29.7	B
	QM-5	Waters	7	1	14.3	28	4.0	14.3	14.3	A
	QM-9	Waters	1	0	0.0	2	0.0	0.0	0.0	A
U049	QM-3	Sediments	9	2	22.2	45	13.5	30.0	26.1	B
	QM-5	Waters	7	0	0.0	28	0.5	1.8	0.9	A
	QM-9	Waters	1	0	0.0	4	2.0	50.0	25.0	A

TABLE 6 (Continued)

Comparison of Laboratory Performance for TMs in Various Studies

Lab No.	Study No.	Matrix	Bias: No. of Parameters Analyzed	Bias: No. of Parameters Biased	Bias: % of Parameters Biased	Flags: No. of Results Reported	Flags: No. of Results Flagged	Flags: % of Results Flagged	Average of % Biased and % Flagged	Comment
U057	QM-3	Sediments	9	2	22.2	45	11.0	24.4	23.3	A
	QM-5	Waters	6	1	16.7	24	2.0	8.3	12.5	A
	QM-9	Waters	1	0	0.0	4	2.0	50.0	25.0	A
U075	QM-3	Sediments	9	2	22.2	45	10.0	22.2	22.2	A
	QM-5	Waters	7	3	42.9	28	10.0	35.7	39.3	B
	QM-9	Waters	1	1	100	4	4.0	100	100	C
U077	QM-5	Waters	7	2	28.6	28	2.0	7.1	17.9	A
	QM-9	Waters	1	0	0.0	4	0.0	0.0	0.0	A
U078	QM-9	Waters	1	0	0.0	4	1.0	25.0	12.5	A
U079	QM-5	Waters	7	0	0.0	28	2.0	7.1	3.6	A
	QM-9	Waters	1	1	100	4	3.5	87.5	93.8	C
U091	QM-5	Waters	7	0	0.0	28	2.0	7.1	3.6	A
	QM-9	Waters	1	0	0.0	4	0.0	0.0	0.0	A
U096	QM-3	Sediments	6	2	33.3	30	24.5	81.7	57.5	C
	QM-5	Waters	5	2	40.0	20	9.5	47.5	43.8	B

TABLE 7

Summary of Relative Performance of Laboratories
for TMs in Sediments

Lab Code	Average of % Biased and % Flagged	Comment
U001	6.1	A
U075	22.2	A
U057	23.3	A
U049	26.1	B
U014	29.7	B
U005	30.0	B
U010	32.5	B
U096	57.5	C

TABLE 8

Summary of Relative Performance of Laboratories for TMs in Waters

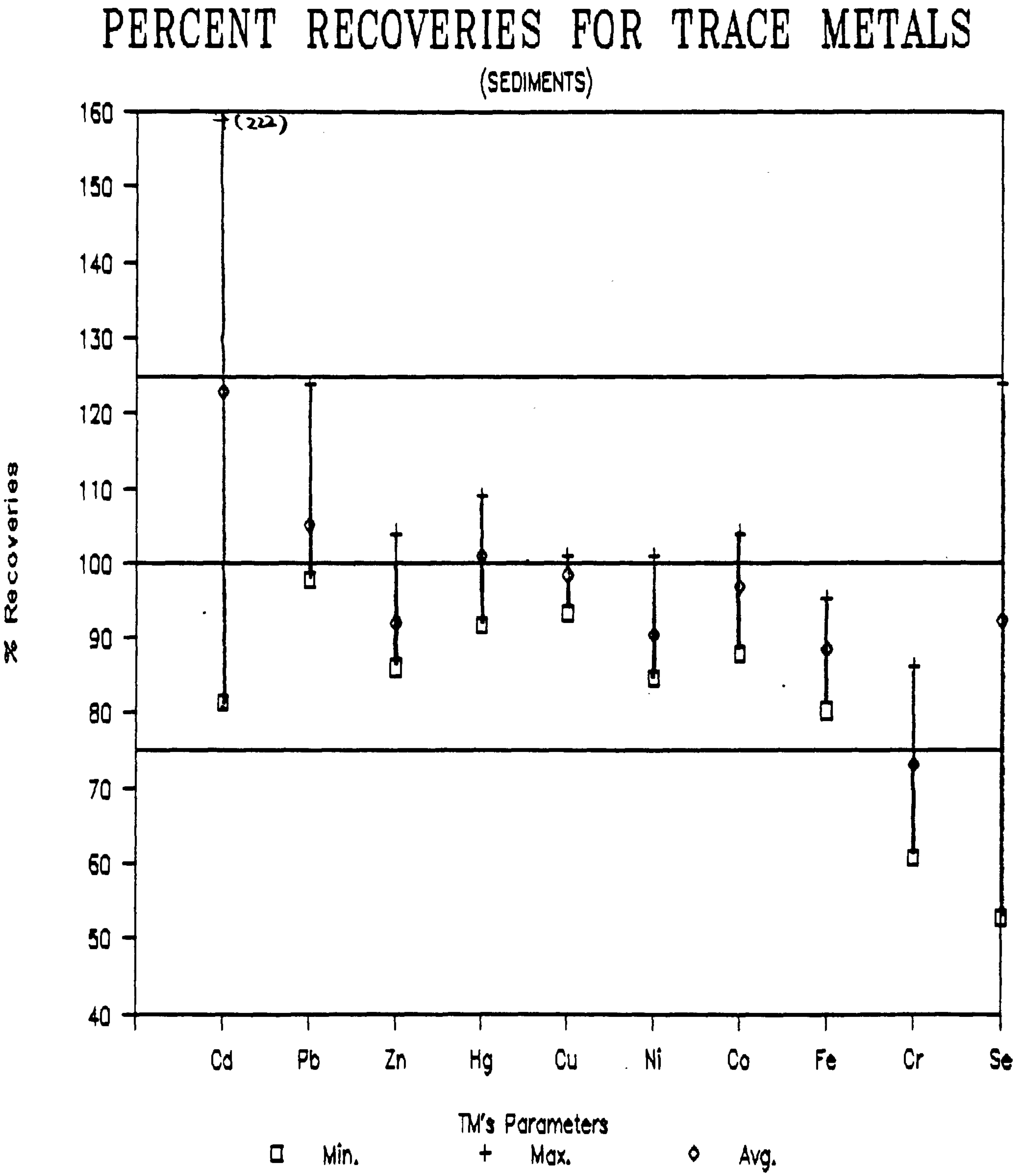
Lab Code	Average of % Biased and % Flagged	Comment
U001A	0.0	A
U001B	0.0	A
U049	0.9	A
U079	3.6	A
U091	3.6	A
U057	12.5	A
U014	14.3	A
U077	17.9	A
U010	20.6	A
U075	39.3	B
U096	43.8	B

TABLE 9

Summary of Relative Performance of Laboratories
for Total Hg in Waters

Lab Code	Average of % Biased and % Flagged	Comment
U001	0.0	A
U014	0.0	A
U077	0.0	A
U091	0.0	A
U078	12.5	A
U049	25.0	A
U057	25.0	A
U079	93.8	C
U075	100	C

Fig. 1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(SEDIMENTS)
(222)
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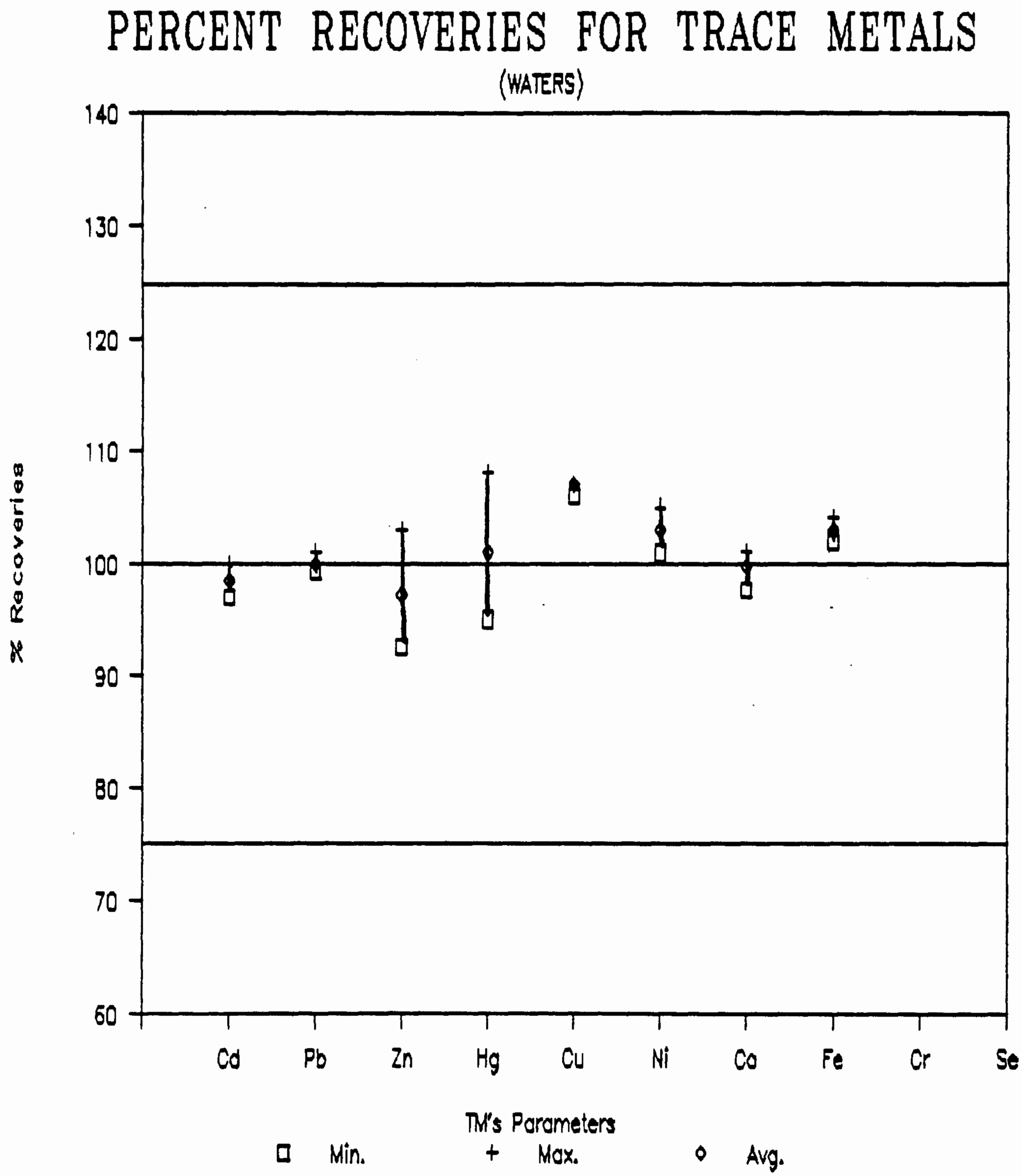
150
140
130
120
110
100
90
80
70
60
50
40
% Recoveries
Cd
Pb
Zn
Hg
Cu
Ni
Co
Fe
Cr
Se
TM's Parameters
Min.
Max.
Avg.

Fig. 2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(WATERS)
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110
100
90
80
70
60
% Recoveries
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Zn
Hg
Cu
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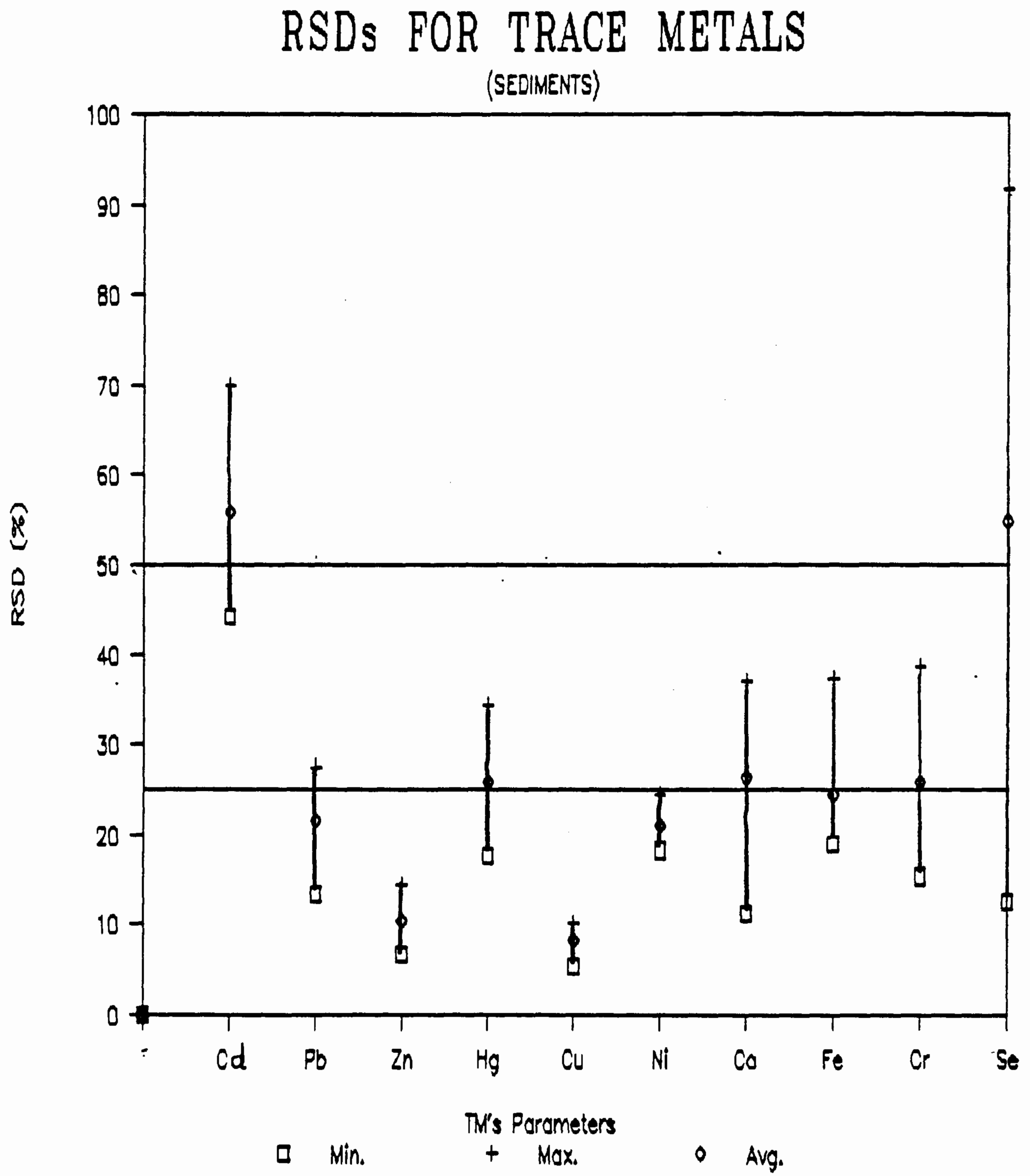
Co
Fe
Cr
Se
TM's Parameters
Min.
Max.
Avg.

Fig. 3


RSDs FOR TRACE METALS
(SEDIMENTS)
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90
80
70
60
50
40
30
20
10
0
RSD (%)
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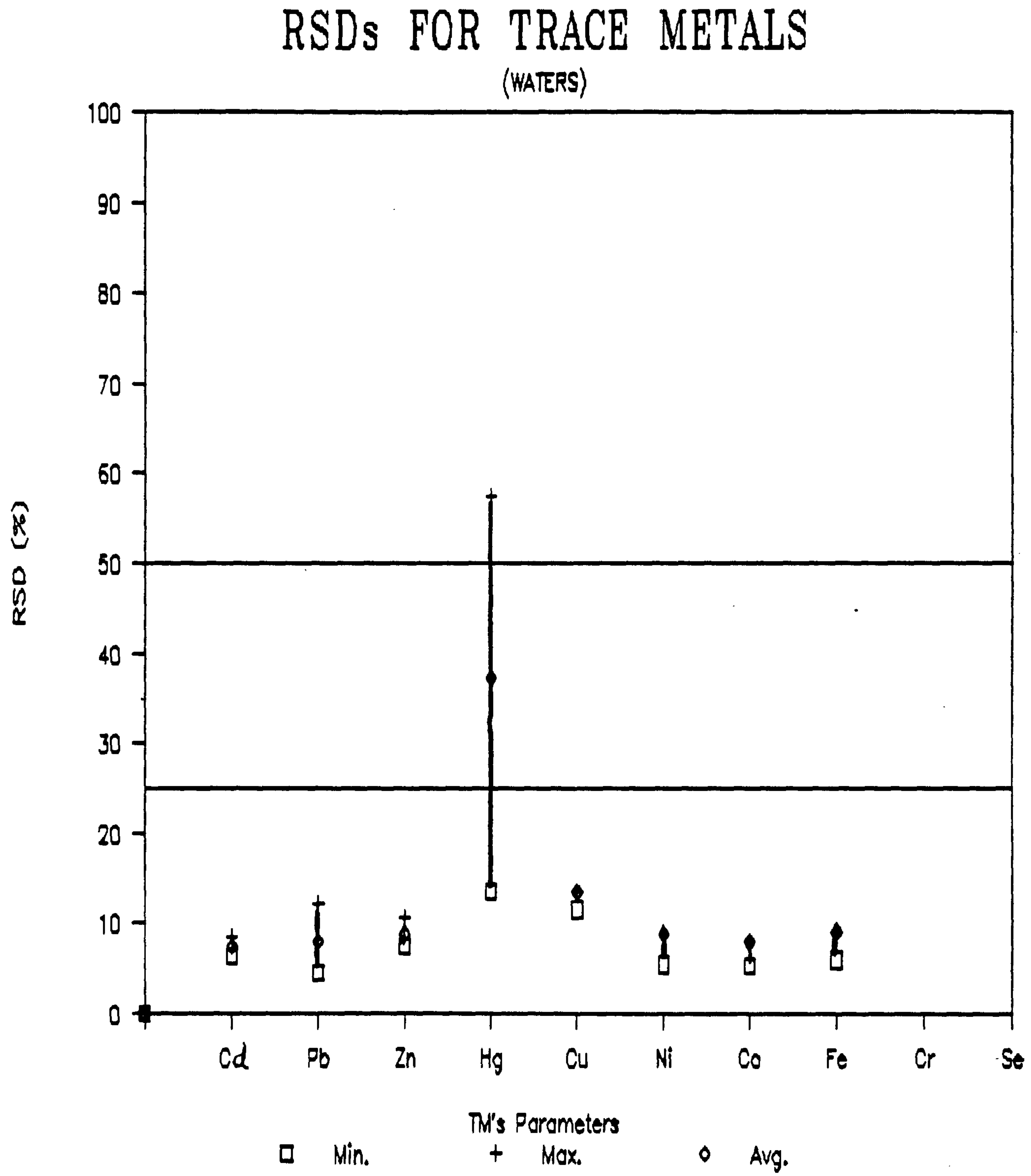
Pb
Zn
Hg
Cu
Ni
Co
Fe
Cr
Se
TM's Parameters
Min.
Max.
Avg.

Fig. 4


RSDs FOR TRACE METALS
(WATERS)
RSD (%)
100
90
80
70
60
50
40
30
20
10
0
Cd
Pb
Zn
Hg
Cu
Ni
Co
Fe
Cr
Se
TM's Parameters
Min.
Max.
Avg.

Appendix I

UGLCCS - FINAL REPORTS

QM-#	TITLE OF FINAL REPORT	AUTHORS
1	PCBs, OCs and CHs in Ampules	W. Horn, R. Szaviola and H.B. Lee and the QMWG
2	PAHs in Ampules	W. Horn, R. Szaviola and H.B. Lee and the QMWG
3	Trace Metals In Sediments	W. Horn, R. Szaviola and H.B. Lee and the QMWG
4	Major Ions In Surface Water	W.A. Horn, R. Szaviola and D. Takeuchi and the QMWG
4	Revised: Major Ions In Surface Water	W.A. Horn, R. Szaviola, D. Takeuchi and P.D. Leishman and the QMWG
5	Trace Metals In Surface Waters	W.A. Horn, D. Takeuchi and R. Szaviola and the QMWG
6	Chlorinated Hydrocarbons In Sediments And Ampules	H.B. Lee, D. Takeuchi and E. Kokotich and the QMWG
7	Chlorinated Hydrocarbons And PCBs In Ampules And Water	R. Szaviola, W. Horn and H.B. Lee and the QMWG
8	Organochlorines In Ampules And Water	R. Szaviola, W. Horn, P. Leishman and H.B. Lee and the QMWG
9	Total Mercury In Surface Water	R. Szaviola, W. Horn and D. Takeuchi and the QMWG
10	PAHs in Ampules and Water	W.C. Li, H.B. Lee and W.A. Horn and the QMWG
11	Total Cyanide In Water	W.C. Li, H.B. Lee and E. Kokotich and the QMWG
12	Total Phenol In Water	W.C. Li, H.B. Lee and E. Kokotich and the QMWG
13	Chlorophenols In Ampules, Fish Oils and Tissues	W.C. Li, R. Szaviola and H.B. Lee and the QMWG

APPENDIX II

Within-lab Precision for Trace Metals

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U001

Parameter	QM-5 (waters)	QM-9 (waters)
	---------------- %	----------------------
Cd		--
Pb		--
Zn		--
Hg	--	29.5 (2)
Cu		--
Ni		--
Co		--
Fe		--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U001A

Parameter	QM-5 (waters)	QM-9 (waters)
	------- % -------	
Cd	0.0 (2)	--
Pb	3.9 (2)	--
Zn	1.4 (2)	--
Hg	--	
Cu	1.0 (2)	--
Ni	1.4 (2)	--
Co	1.0 (2)	--
Fe	0.8 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U001B

Parameter	QM-5 (waters)	QM-9 (waters)
	---------------- %	----------------------
Cd	0.4 (2)	--
Pb	5.6 (2)	--
Zn	1.3 (2)	--
Hg	--	
Cu	0.4 (2)	--
Ni	0.4 (2)	--
Co	0.7 (2)	--
Fe	0.3 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U010

Parameter	QM-5 (waters)	QM-9 (waters)
	---------------- %	----------------------
Cd	0.4 (2)	--
Pb	3.7 (2)	--
Zn	0.0 (2)	--
Hg	--	16.7 (2)
Cu	0.0 (2)	--
Ni	1.9 (2)	--
Co	0.0 (2)	--
Fe	3.8 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U014

Parameter	QM-5 (waters)	QM-9 (waters)
	%	
Cd	0.0 (2)	--
Pb	0.0 (2)	--
Zn	5.7 (2)	--
Hg	--	0.0 (1)
Cu	0.4 (2)	--
Ni	0.5 (2)	--
Co	2.4 (2)	--
Fe	6.7 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U049

Parameter	QM-5 (waters)	QM-9 (waters)
	----------------- %	-----------------------
Cd	1.3 (2)	--
Pb	4.5 (2)	--
Zn	6.1 (2)	--
Hg	--	3.0 (2)
Cu	7.7 (2)	--
Ni	0.0 (2)	--
Co	0.0 (2)	--
Fe	0.0 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U057

Parameter	QM-5 (waters)	QM-9 (waters)
	---------------- %	----------------------
Cd	3.1 (2)	--
Pb	2.4 (2)	--
Zn	NA	--
Hg	--	16.6 (2)
Cu	1.5 (2)	--
Ni	4.5 (2)	--
Co	1.8 (2)	--
Fe	4.2 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U075

Parameter	QM-5 (waters)	QM-9 (waters)
	%	%
Cd	1.0 (2)	--
Pb	2.4 (2)	--
Zn	3.8 (2)	--
Hg	--	8.4 (2)
Cu	1.1 (2)	--
Ni	2.3 (2)	--
Co	4.1 (2)	--
Fe	27.7 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U077

Parameter	QM-5 (waters)	QM-9 (waters)
	%	
Cd	0.8 (2)	--
Pb	0.9 (2)	--
Zn	2.5 (2)	--
Hg	--	0.0 (2)
Cu	4.2 (2)	--
Ni	3.3 (2)	--
Co	0.7 (2)	--
Fe	1.1 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U078

Parameter	QM-5 (waters)	QM-9 (waters)
	---------------- %	----------------------
Cd		--
Pb		--
Zn		--
Hg	--	27.1 (2)
Cu		--
Ni		--
Co		--
Fe		--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U079

Parameter	QM-5 (waters)	QM-9 (waters)
	------------ % ------------	
Cd	8.5 (2)	--
Pb	2.5 (2)	--
Zn	3.5 (2)	--
Hg	--	4.7 (2)
Cu	4.1 (2)	--
Ni	2.5 (2)	--
Co	7.8 (2)	--
Fe	4.7 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U091

Parameter	QM-5 (waters)	QM-9 (waters)
	---------- % ----------	
Cd	1.3 (2)	--
Pb	5.6 (2)	--
Zn	1.4 (2)	--
Hg	--	2.7 (2)
Cu	0.8 (2)	--
Ni	3.7 (2)	--
Co	1.2 (2)	--
Fe	6.8 (2)	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

Within-lab Precision for Trace Metals
(Avg. RSD)

Lab Code: U096

Parameter	QM-5 (waters)	QM-9 (waters)
	%	
Cd	3.7 (2)	--
Pb	NA	--
Zn	0.0 (2)	--
Hg	--	
Cu	0.0 (2)	--
Ni	0.0 (2)	--
Co	0.0 (2)	--
Fe	NA	--
Cr	--	--
Se	--	--

Note: The numbers in parentheses are the number of duplicate pairs.

APPENDIX III

Glossary of Terms

(1) Ranking

Ranking is a non-parametric statistical technique used for the detection of pronounced systematic error (bias) in interlaboratory studies. According to Youden's procedure, rank 1 is given to the laboratory that provided the lowest result, rank 2 to the next lowest. In case of a tie, the average rank is given to the tied laboratories. Results with a < sign are not ranked. For each parameter, the total rank of each laboratory is the sum of individual ranks on each sample. In the case of six test samples and ten laboratories, the 5% probability limits for ranking scores are 14 and 52. A laboratory with a score lower than 14 is identified as biased low. Similarly, a laboratory with a total rank higher than 52 is biased high. In both cases, their results are classified as outliers. In cases where a laboratory did not provide all the results, or some of the results were not ranked, the average rank instead of total rank was used for the determination of biased statements.

The more comparable, i.e. better, laboratories should have ranks in the middle rather than at the extreme ends. However, laboratories with middle ranks do not necessarily mean that they provide more consistent results since very high results (high ranks) and very low results (low ranks) would average out to yield a total rank close to the median. Therefore, ranking alone is not sufficient to determine the performance of a laboratory.

(2) Flagging

When the true values of constituents in test samples are unknown, individual results can be evaluated in terms of their absolute differences from the interlaboratory medians. Medians and in some cases design values are chosen rather than means since they are not influenced by a moderate number of extreme values. By this flagging technique, all results are graded into the following three groups in the order of decreasing accuracy: (1) results with no flags, (2) results with H or L flags, and (3) results with VH or VL flags. Before evaluation is performed, three parameters, namely, Lower Limit for use of Basic Acceptable Error (LLBAE), Basic Acceptable Error (BAE), and Concentration Error Increment (CEI) are to be set. LLBAE is usually set at the lower end of the medians in the test samples. A 20-25% error at LLBAE is considered reasonable and thus this is used as BAE. For samples whose medians are at or below LLBAE, the results are evaluated according to the following formulae:

	Absolute difference between sample and median results	$\leq$ BAE	: acceptable
BAE <	Absolute diffence between sample and median results	$\leq$ 1.5 x BAE	: H or L
	Absolute difference between sample and median results	> 1.5 x BAE	: VH or VL

For samples whose medians are above the LLBAE, the allowable BAE is augmented by adding an increment to the BAE. This increment is calculated by multiplying the CEI by the difference between the sample median and LLBAE values. In this study, CEI is set at 0.1. Sample results are again evaluated by the above three formulae except that the augmented BAE is used instead of BAE.

For futher discussion on this evaluation technique, please refer to the original paper by Clark.

Bias: A set of results is said to be biased when the set exhibits a tendency to be either higher or lower than some standard - the standard which has been used in the analysis of our studies thus far has been the performance of all other participating laboratories. The ranking procedure employed in testing for bias is described in W.J. Youden's paper, "Ranking Laboratories by Round-Robin Tests" from Precision Measurement and Calibration, H.H. Ku, Editor, NBS Special Publication 300 - Volume 1, U.S. Government Printing Office, Washington, D.C., 1969. In this paper, Youden establishes the rationale for evaluating laboratories' performance by ranking results. In our use of the procedure there is about 1 chance in 20 of deeming a set of results biased when in fact it is not, that is, $^{t} = 0.05$.

Codes

W: A "W" code is used with a reported result when no measurement was possible due to no response of the instrument to the sample. The "W" is preceded by the smallest determinative division that can be used in the units used in reporting.

T: The "T" code is used with values between the Criterion of Detection and the "W" value. The Criterion of Detection is commonly thought of by many as the limit of detection.

NA:	not analyzed		
NRA:	not routinely analyzed		
N or ND:	not detected		
NAPP:	not applicable		
H:	high	VH:	very high
L:	low	VL:	very low

APPENDIX IV

Lab-Specific Appraisal for Bias and Flag Statements

(Trace Metals)

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U001

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd	LT	LT				
Pb	S	1 VH				
Zn	S	-				
Hg	S	1 H			S	-
Cu	S	-				
Ni	-	1 H;1 L;2 VL				
Co	LT	LT				
Fe	S	1 H				
Cr	S	-				
Se	S	-				

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U001A

Parameter	QM-3 (sediments) Bias	QM-3 (sediments) Flag	QM-5 (waters) Bias	QM-5 (waters) Flag	QM-9 (waters) Bias	QM-9 (waters) Flag
Cd			S	-		
Pb			S	-		
Zn			S	-		
Hg						
Cu			S	-		
Ni			S	-		
Co			S	-		
Fe			S	-		
Cr						
Se						

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U001B

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd			S	-		
Pb			S	-		
Zn			S	-		
Hg						
Cu			S	-		
Ni			S	-		
Co			S	-		
Fe			S	-		
Cr						
Se						

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U005

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd	-	1 VH;1 L;2 VL				
Pb	S	-				
Zn	-	1 VH				
Hg	H	3 VH;1 H				
Cu	S	-				
Ni	S	1 VL				
Co	S	2 L				
Fe	L	1 L;4 VL				
Cr	S	2 L;3 VL				
Se	S	1 L;1 VL				

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U010

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd	S	4 L	S	-		
Pb	L	4 VL	H	1 VH		
Zn	S	1 L	S	1 VH;2 H		
Hg	S	-			S	1 VL
Cu	S	-	S	-		
Ni	S	-	H	-		
Co	S	-	S	-		
Fe	S	2 L	S	1 H		
Cr	L	5 VL				
Se	H	5 VH				

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U049

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd	H	5 VH	S	-		
Pb	H	2 VH;2 H	S	1 L		
Zn	S	1 VH	S	-		
Hg	S	1 H			S	1 VH;2 H
Cu	S	-	S	-		
Ni	S	-	S	-		
Co	S	1 VH;1 H	S	-		
Fe	S	-	S	-		
Cr	S	1 L;2 VL				
Se	NA	NA				

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U014

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd	S	1 L;1 VL	S	-		
Pb	L	3 L;1 VL	S	2 VL		
Zn	L	2 L	S	-		
Hg	S	-			S	-
Cu	L	-	S	-		
Ni	S	1 L;1 VL	S	-		
Co	S	3 L	S	-		
Fe	S	3 L;1 VL	H	2 VH		
Cr	S	2 L;2 VL				
Se	S	-				

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U057

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd	L	1 L;4 VL	S	-		
Pb	S	-	NA	NA		
Zn	S	-	S	-		
Hg	L	1 L;3 VL			S	2 L;1 VL
Cu	S	-	S	-		
Ni	S	-	S	3 L		
Co	S	2 L;1 VL	S	-		
Fe	S	1 H	L	1 L		
Cr	S	1 L				
Se	NA	NA				

Lab-Specific Appraisal for Bias and Flag Statements (Trace Metals)

Lab Code: U075

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd	S	1 VH;1 L	S	-		
Pb	S	-	S	-		
Zn	S	1 H	H	3 VH;1 H		
Hg	S	2 L			L	4 VL
Cu	H	1 H	H	2 VH;2 H		
Ni	S	1 VH;4 H	S	-		
Co	S	2 VH	S	1 VH;1 H		
Fe	H	3 H	H	2 VH		
Cr	S	-				
Se	NA	NA				

Lab-Specific Appraisal for Bias and Flag Statements (Trace Metals)

Lab Code: U077

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd			S	-		
Pb			S	-		
Zn			S	-		
Hg					S	-
Cu			H	2 VH		
Ni			H	-		
Co			S	-		
Fe			S	-		
Cr						
Se						

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U078

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd						
Pb						
Zn						
Hg					S	1 VH
Cu						
Ni						
Co						
Fe						
Cr						
Se						

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U079

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd			S	-		
Pb			S	-		
Zn			S	1 VL		
Hg					H	3 VH;1 H
Cu			S	1 L		
Ni			S	-		
Co			S	-		
Fe			S	1 L		
Cr						
Se						

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U091

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd			S	-		
Pb			S	1 L		
Zn			S	-		
Hg					S	-
Cu			S	2 L		
Ni			S	-		
Co			S	-		
Fe			S	1 H		
Cr						
Se						

Lab-Specific Appraisal for Bias and Flag Statements
(Trace Metals)

Lab Code: U096

Parameter	QM-3 (sediments)		QM-5 (waters)		QM-9 (waters)	
	Bias	Flag	Bias	Flag	Bias	Flag
Cd	S	5 VH	L	4 VL		
Pb	NA	NA	NA	NA		
Zn	-	3 VH;2 VL	S	1 L		
Hg	NA	NA				
Cu	S	1 L	S	-		
Ni	H	5 VH	L	4 VL		
Co	H	4 VH	S	2 L		
Fe	NA	NA	NA	NA		
Cr	-	4 VH;1 VL				
Se	NA	NA				